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# Phenomenon of embrittlement in titanium shells from hydrogen exposure

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**Abstract.** Increasing the reliability of equipment used for production, transportation, storage and utilization of hydrogen is directly related to solving the problem of hydrogen embrittlement of metals. Without a fundamental physical theory, it is necessary to predict the bearing capacity of metal structures on the basis of obtained experimental data on the effect which hydrogen have on metal properties. This paper presents a solution (based on the method of discrete orthogonalization proposed by S.K. Godunov) of a physically-nonlinear problem of stress distribution in a titanium shell. Since hydrogen, most notably, reduces plastic properties of metals utilized in structural elements, a critical point was determined where the intensity of shear deformation is maximal. It was found how the intensity changes at a critical point of a shell if the pressure within the device rises to an emergency level. Such a rise of the pressure in the shell could lead to appearance of plastic deformation regions, and hydrogen exposure is manifested in reduced breaking stress and changed fracture pattern.

## 1. Introduction

Negative effect which corrosive medium has on mechanical properties of metals used in structural elements is one of the major factors determining designed and remaining service lives of many potential-accident objects. For example, hydrogen exposure, as a rule, leads to reduction of all mechanical properties of steels and alloys. Thus, assessing strengths of various structures utilized in hydrogenous media requires mathematical models to be developed, which would be based on obtained experimental data showing hydrogen effect on metals. The goal of the research was to analyze the effect which hydrogen saturation has on the bearing capacity of a titanium shell structure.

Since the problems of hydrogen interaction with metals and alloys have been studied from the beginning of the last century, the result is a lot of theoretical and experimental material collected, from which only modern sources were referred to – as in [1, 2, 3] which cite monographs and papers on the topic in question. And it should also be reminded that hydrogen interaction with titanium alloys could change their mechanical properties both in a positive and negative manner [4, 5].

Hydrogen effect on a titanium alloy was recorded in experiments where tension was applied to specimens, manifested in changes of stress-strain diagram properties. The relation between the stress  $\sigma$ , strain  $\varepsilon$  and hydrogen concentration  $c$  in a mechanically loaded structural element used in a hydrogenous medium could be defined by time period  $t$  and expressed as  $\sigma = f(\varepsilon, c, t)$ . Therefore, to



evaluate the stress state of a structural element one needs to apply methods of computational and experimental mechanics.

## 2. Problem formulation and permissive equations

The paper presents an approach to determining the stress state of a thin-walled structure taking metal embrittlement into account. The structure is supposed to be a titanium shell of revolution,  $h$  in width, with variable geometric and mechanical properties along a generating line. The shell could be considered as a continuous mid-surface with curvilinear orthogonal coordinates  $s, \theta, \gamma$ , where  $s$  and  $\theta$  are, correspondingly, meridional and peripheral coordinates,  $\gamma$  is direction of an outer normal to the shell surface. Therefore, we have  $-h/2 \leq \gamma \leq h/2$ . The inner surface of the shell is in direct contact with a corrosive hydrogenous medium of excessive pressure  $p$ , which lead to hydrogen diffusion into the shell.

The stress state of a thin structure would be assessed using the classical theory of shells in a geometrically linear and physically nonlinear formulation. In its general form, a solution of such a bound nonstationary problem could be presented as the following sequence: 1) solving the problem of hydrogen diffusion while determining distribution of hydrogen concentration  $c(t)$ ; 2) carrying out an experiment and obtaining relations between stress  $\sigma$ , strain  $\varepsilon$  and hydrogen concentration  $c$  for a uniaxial stress state of a specimen –  $\sigma = f(c, \varepsilon)$ ; 3) determining the stress state of the shell while taking physical and mechanical properties of a structural material into account –  $\sigma = f(c, p)$ .

It is known that the diffusion equation is completely identical to the heat conduction one [6, 7, 8]. Thus, the methods of solving the problems of diffusion and heat conduction are the same. Therefore, a differential diffusion equation, by analogy to a differential heat conduction equation and in consideration of a lack of heat sources for a thin shell, could expressed in the form of [9, 10]

$$\frac{1}{H_1 H_2} \left[ \frac{\partial}{\partial s} \left( \frac{H_2}{H_1} \frac{\partial c}{\partial s} \right) + \frac{\partial}{\partial \theta} \left( \frac{H_1}{H_2} \frac{\partial c}{\partial \theta} \right) + \frac{\partial}{\partial \gamma} \left( H_1 H_2 \frac{\partial c}{\partial \gamma} \right) \right] = \frac{1}{D} \frac{\partial c}{\partial t}, \quad (1)$$

where  $D$  – diffusion coefficient,  $H_1, H_2$  – Lamé parameters.

The boundary conditions for the problem in question would be represented by values of hydrogen concentration  $c$ , which should be known for a shell surface if one considers certain physical aspects [6]. If one makes a conjecture about fast mixing of the hydrogen medium, then boundary conditions of the first kind could defined as

$$c \left( \gamma = -\frac{h}{2}, t \right) = c_H \quad (2)$$

where  $c_H$  – initial hydrogen concentration on the shell surface.

It is known that titanium alloys interact quite actively with hydrogen – its solubility reaching 40000 ppm, which is by a factor of a hundred or thousand higher than in the case of steel [11, 12].

When Kirchhoff–Love hypothesis are used, an axisymmetric stress state of thin-walled structures is expressed by a system of ordinary differential sixth-order equations [9, 10, 13, 14]

$$\frac{d\bar{Y}}{ds} = P_{ij} \bar{Y} + \bar{f}, \quad (i, j = 1, 2, \dots, 6), \quad (3)$$

$$\bar{Y} = \{N_r, N_z, M_s, u_r, u_z, \vartheta_s\},$$

with boundary conditions

$$\begin{aligned}
B_1 \bar{Y}(s_0) &= \bar{b}_1 \\
B_2 \bar{Y}(s_L) &= \bar{b}_2,
\end{aligned} \tag{4}$$

where  $N_r, N_z$  are radial and axial forces;  $u_r, u_z$  – similar shears,  $M_s$  – meridional torque;  $\mathcal{G}_s$  – normal inclination angle. The elements of matrix  $P_{ij}$  and column vector of absolute terms  $\bar{f}$  are not cited here because they are too large.  $B_1$  and  $B_2$  are given matrices;  $\bar{b}_1$  and  $\bar{b}_2$  – given vectors.

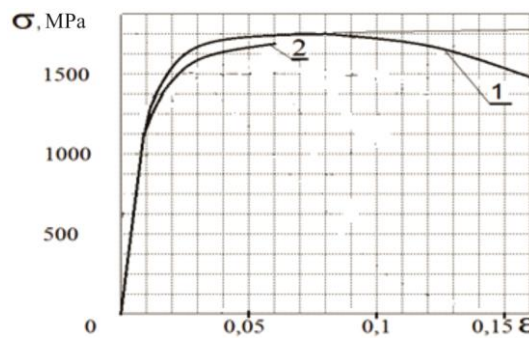
### 3. Computational and experimental methods of solving the problem

For the purposes of solving the diffusion problem, we use methods developed to solve boundary problems of heat conduction. Those problems adopt an approach which requires the heat conduction equation to be substituted with an equivalent variational equation [10] solved by the finite-element method.

After a solution of equation (1) under boundary conditions (2) has been found, one can determine hydrogen concentration distribution over shell width  $c(r, t)$  at any given moment. The results of a computational solution of such a diffusion problem for a steel shell structure are cited in [15,16]. To solve the problem in (3), we use experimental data on specimens of VT20 titanium alloy.

In that experiment titanium hydride was utilized as a hydrogen source to achieve hydrogen saturation of a titanium plate. Then, specimens of 2 mm both in diameter and length of their working parts were prepared to carry out tensile tests. And a loading device of high rigidity with parallel pulls [17] was used in those tests on such small specimens.

Figure 1 shows conditional diagrams of tension applied to a specimen made from a plate in its initial state (curve 1) and a hydrogen-saturated plate (curve 2).



**Figure 1.** Conditional stress-strain diagrams for VT20 alloy.

Since various existing methods of evaluating hydrogen content in titanium alloys require special expensive equipment [18], hydrogen concentration in specimens utilized in the experiment could not have been found. To solve the problem, given conditional dependencies were reformed into true tension diagrams and approximated by the following discrete expression:

$$\begin{aligned}
\varepsilon_1=0,0 \quad \varepsilon_2=0,01 \quad \varepsilon_3=0,03 \quad \varepsilon_4=0,05 \quad \varepsilon_5=0,07 \quad \varepsilon_6=0,16 \quad \text{при } c=0, \\
\sigma_1=0,0 \quad \sigma_2=1100 \quad \sigma_3=1600 \quad \sigma_4=1690 \quad \sigma_5=1700 \quad \sigma_6=1710
\end{aligned} \tag{5}$$

$$\begin{aligned}
\varepsilon_1=0,0 \quad \varepsilon_2=0,01 \quad \varepsilon_3=0,03 \quad \varepsilon_4=0,05 \quad \varepsilon_5=0,06 \quad \text{при } c \neq 0, \\
\sigma_1=0,0 \quad \sigma_2=1100 \quad \sigma_3=1550 \quad \sigma_4=1640 \quad \sigma_5=1660
\end{aligned} \tag{6}$$

The observed reduction in ultimate strength of an alloy is typical of many titanium alloys [19]. Let us prove that the reduction of available material plasticity (which is determined by the length of a stress-strain diagram) significantly impacts the bearing capacity of a structure. To solve the system of equations in (3) under boundary conditions (4), the method of discrete orthogonalization proposed by S.K. Godunov [20] was used. This method «smooths» the boundary effects and is usually applied when solving various problems of the theory of shells [10, 13, 14, 21].

To solve this one in the context of possible plastic deformation, a physically nonlinear problem would be expressed by the system of differential equations in (3), with a relation between stress and strain linearized by the method of additional strains. The relation is expressed in the form of Hooke's law, but with additional equation members introduced to factor in the dependence of mechanical properties of a material on deformation and temperature [10]. Assume that such a relation would also take into account the dependence of the mechanical properties on hydrogen concentration. Then, a volumetric stress state of a shell could be contrasted against a uniaxial state in the case of simple tension applied to specimens when  $C = \text{const}$  [10]

$$S_{\sigma}^* = \frac{\sigma}{\sqrt{3}}, \quad T^* = \frac{1+\nu}{\sqrt{3}} \varepsilon, \quad (7)$$

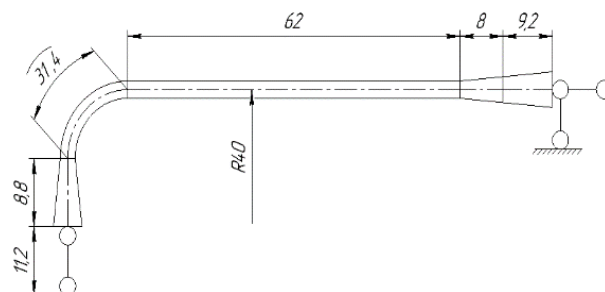
where  $\sigma$  and  $\varepsilon$  are stresses and strains in the case of simple tension applied to specimens, and  $\nu$  is Poisson's ratio. Intensities of tangent stresses and shear strains in a shell  $S_{\sigma}$  and  $T$  are determined as

$$S_{\sigma} = \sqrt{(1/3) \cdot (\sigma_s^2 - \sigma_s \sigma_g + \sigma_g^2)}, \quad T = \sqrt{(1/6) \cdot [(\varepsilon_s - \varepsilon_g)^2 + (\varepsilon_g - \varepsilon_n)^2 + (\varepsilon_n - \varepsilon_s)^2]} \quad (8)$$

where  $\sigma_s$  and  $\sigma_g$  are, correspondingly, meridional and peripheral stresses, and  $\varepsilon_s, \varepsilon_g, \varepsilon_n$  – components of stresses by meridian, periphery and normal to the shell surface.

#### 4. Solution example

As an example, the stress state of a thin-walled body of a special-purpose technical object made of titanium alloy VT20 was determined. The thin-walled body was approximated by 5 shell elements: plate  $0 \leq s \leq 0,088$  m, torus  $0,088 \leq s \leq 0,40216$  m and 3 cylindrical sections of various widths (figure 2). The body wall width is mostly  $h=0,018$  m, the median radius of its cylindrical section  $R=0,4$  m. The body is under internal pressure of  $P=3,2$  MPa, at operational temperature of  $20^\circ\text{C}$ . When calculations were made, mechanical properties of the body were expressed by dependencies without hydrogen present (5) and with hydrogen saturation (6). Boundary conditions (4) reflected perfectly actual workings of the body: there is a hinged movable support at the left end, and a hinged immovable one at the right end.

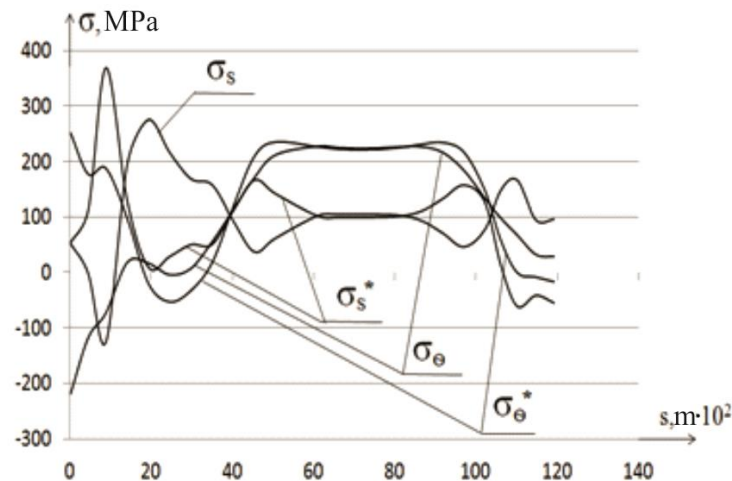


**Figure 2.** Object body (sizes in centimeters).

It was unnecessary to solve the problem of hydrogen diffusion into a thin-walled body and determine the law of hydrogen concentration distribution over the width of the titanium shell since the

concentration under hydrogen saturation in the experiment on uniaxial tension were not carried out. The methods of solving such problems are discussed in detail in [15, 16].

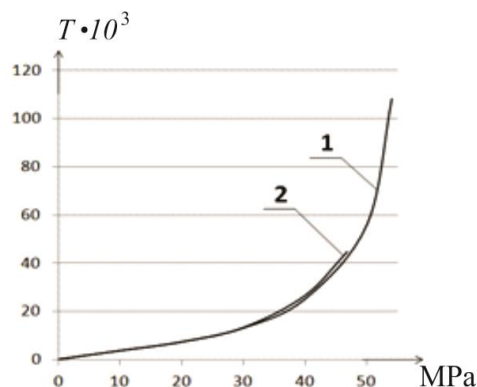
Figure 3 shows distribution of meridional  $\sigma_s$  and peripheral  $\sigma_\theta$  stresses by components along coordinate  $s$  on the inner shell surface. The asterisk denotes the stresses on the outer shell surface. It follows from the calculation results that, for given mechanical properties in (5) and (6) under pressure of  $P=10$  MPa, the shell material remains in the elastic region of the diagram.



**Figure 3.** Changes of meridional  $\sigma_s$  and peripheral  $\sigma_\theta$  stresses along coordinate  $s$  on the inner and outer shell surfaces.

Further pressure increase makes the problem physically nonlinear. For example, under pressure of  $P=30$  MPa, 5 approximations are required to solve such a nonlinear problem and obtain the necessary solution accuracy of 1% for given mechanical properties expressed by (5), and 6 approximations for (6). And it leads to appearance of plastic deformation regions.

Figure 4 shows how intensity  $T$ , calculated using formula (8), changes with the pressure increase at a maximally-stressed point of the shell ( $s=0,088$  m). Curve 1 corresponds to calculations for given mechanical properties expressed by (5), and curve 2 for (6). The figure demonstrates (curve 2) that the ultimate pressure which would break a shell made of hydrogen-saturated material is  $P=46,9$ , which corresponds to intensity of breaking deformations for a specimen  $T^*$  calculated using expression (7). The plastic properties of a hydrogen-unsaturated material (curve 1) help the shell to withstand much higher pressure of  $P=54,6$  MPa.



**Figure 4.** Changes of shear deformation intensity  $T$  on the outer shell surface.

Similar calculations which factor in the embrittlement of a titanium alloy under hydrogen saturation predict substantial (by 14%) reduction of the ultimate breaking pressure of a shell structure.

## 5. Conclusion

Thus, using modern computational and experimental methods, a solution was obtained of a physical-mechanical problem of calculating the stress state of a thin-walled shell made of titanium alloy under mechanical loading and hydrogen exposure. Existing stresses and their invariants are determined by solving a physically nonlinear boundary problem. It is shown that a known effect of titanium alloy embrittlement observed in an experiment on specimens under hydrogen impact is manifested in a shell structure by substantial reduction (14%) of the ultimate pressure.

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